Dynamics of the Destruction and Rebuilding of a Dipole Gap in Glasses

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After a strong electric bias field was applied to a glass sample at temperatures in the millikelvin range its AC-dielectric constant increases and then decays logarithmically with time. For the polyester glass mylar we have observed the relaxation of the dielectric constant back to its initial value for several temperatures and histories of the bias field. Starting from the dipole gap theory we have developed a model suggesting that the change of the dielectric constant after transient application of a bias field is only partly due to relaxational processes. In addition, non-adiabatic driving of tunneling states (TSs) by applied electric fields causes long lasting changes in the dielectric constant. Moreover, our observations indicate that at temperatures below 50 mK the relaxation of TSs is caused primarily by interactions between TSs.

At low temperatures the internal energy of glasses is vastly elevated by atomic tunneling states (TSs) and most properties of amorphous solids are strongly influenced by these additional degrees of freedom [1, 2]. The phenomenological 'tunneling model' describes the thermal, elastic and dielectric properties of glasses at low temperatures successfully [3, 4]. Starting from the central assumption that the potential minima of groups of atoms are not well defined, it describes such a configuration by a 'particle' moving in a double well potential. The two identical and harmonic wells may differ in depth by the asymmetry energy Δ. At low temperatures only the energy ground states of the two wells are occupied and the TSs oscillate by quantum mechanical tunneling between them. The energy splitting of these two-level systems is given by $E_0 = \sqrt{\Delta_0^2 + \Delta^2}$, where Δ_0 is the tunneling splitting. The parameters Δ_0 and Δ are widely distributed due to the randomness of the glassy structure.

Soon after the introduction of the tunneling model in 1972 it was shown that the mutual interaction of TSs causes spectral diffusion, while interaction that involves energy exchange between TSs was long believed to be unimportant. However, more recent experiments revealed deviations from the tunneling model and indicate that for many properties the interaction between TSs gains importance with decreasing temperature [5, 6].

Here we will concentrate on the effects of electric bias fields on the low temperature AC-dielectric constant of amorphous materials. A sudden large change of the electric bias field causes the relative dielectric constant $\delta\epsilon/\epsilon$ of a glass sample, that was originally in thermal equilibrium, to immediately change to a larger value and then decay back to its initial value logarithmically for several decades in time. In addition, a relatively slow sweep of the bias field reveals a minimum of $\delta\epsilon/\epsilon$ at the initial bias field, in our case at zero field [6]. A. Burin explained these findings within a 'dipole gap' model, which considers the weak dipole-dipole interaction $J_{ij} = U_0/r_{ij}^3$ between TSs [7]. Although the interaction is weak, some

TSs fulfill the condition $J_{ij} \gtrsim (E_{0i} + E_{0j})$ for strongly coupled pairs. Within the dipole gap model, such strongly coupled TSs form clusters that do not contribute fully to the dielectric constant because their individual dipole moments are pinned relative to each other. A change of the bias field alters the distribution of asymmetry energies and leads to the formation of new clusters of strongly coupled TSs. As long as the new clusters remain out of thermal equilibrium, their TSs contribute fully to the dielectric constant [7]. This explains the observed minimum of $\delta\epsilon/\epsilon$ at the initial bias field. In addition mutual interaction of TSs leads to a new relaxation channel [8] due to resonant energy exchange between pairs of TSs resulting in the overall relaxation rate

$$\tau^{-1} = \gamma_0 \Delta_0^2 E \coth\left(\frac{E}{2k_B T}\right) + \alpha_0 \frac{\Delta_0^2}{E^2} k_B T , \quad (1)$$

consisting of the well known one-phonon relaxation rate (first term r.h.s.) and the contribution due to interaction. The material constants γ_0 [9] and α_0 [8] depend on the coupling of the TSs to phonons and between each other respectively. Note that the dynamics of TSs that generate any change in the dielectric constant is dominated by thermally active TSs that fulfill $E = \sqrt{\Delta_0^2 + (\Delta + \mathbf{p} \cdot \mathbf{F})^2} \sim k_B T$ producing an additional temperature dependence in (1) implicit in the energy splittings E. Moreover, after changing the bias field $\mathbf{F}$ by more then $\mathbf{p} \cdot \delta\mathbf{F} \sim k_B T$, where $\mathbf{p}$ is the dipole moment of the TSs, a different set of TSs fulfills $E \sim k_B T$. Therefore in past experiments in which a large bias field was suddenly applied to study the dynamics of strongly coupled clusters the formation of a new dipole gap consisting of different clusters than those formed at zero field was observed. The interpretations of these measurements relied on assumptions such as a flat energy distribution of TSs for $E_0 \lesssim \mathbf{p} \cdot \mathbf{F} \equiv \Phi$.

All our measurements were made at zero bias field. Thus we always measured the same set of TSs. However, we applied a large electric bias field $\Phi \gg k_B T$ for the

waiting time t_w to destroy the zero field dipole gap and then observed the restoration of the same dipole gap by measuring $\delta\epsilon/\epsilon$ in zero field. In addition, we took care to linearly sweep the bias field up and down in the same sweep time t_s.

As long as the bias field is applied the TSs are relaxing towards a new equilibrium, thereby breaking clusters of TSs that were initially strongly coupled. Back at zero bias field these clusters rearrange. The TS's relaxation times depend according to (1) on their asymmetry energies and are broadly distributed. For $\Phi \gg k_B T$ initially thermal TSs with $E_0 \sim k_B T$ have $E \sim \Phi$ at the bias field **F**. We introduce the decay time τ_0 at which we expect the dielectric constant to again reach its initial value, i.e. $\epsilon(t) = \epsilon(\infty)$ before the bias field was applied

$$\frac{\tau_0}{t_w} = \frac{\tau(E = k_B T)}{\tau(E = \Phi)} \simeq \left(\frac{k_B T}{\Phi}\right)^2 \frac{(\gamma_0 \Phi^3 + \alpha_0 k_B T)}{2.2\gamma_0(k_B T)^3 + \alpha_0 k_B T} . \tag{2}$$

For this we assumed that both the destruction and restoration of the dipole gap are solely caused by relaxational processes, thus that τ_0 is given by the ratio of the relaxation times of TSs without and with field times the waiting time. Following the dipole gap theory we obtain for the change of the dielectric constant, after a bias field **F** was applied for a time t_w,

$$\delta\epsilon/\epsilon \simeq 2P_0 \frac{2p^2}{3\varepsilon_0\varepsilon} \frac{P_0 U_0}{2} \frac{2\pi}{3} \left[\ln\left\{\frac{\Phi}{k_B T}\right\}\right]^2 \ln\left\{\frac{\tau_0}{t}\right\} . \tag{3}$$

Since in (3) relaxational processes are approximated by Heaviside step functions we expect deviations from logarithmic decays at the start and the end of the decay.

Our experiments were performed on $15\mu m$ thick mylar film (amorphous polyester) at a frequency of 10 kHz at temperatures well below the minimum of $\delta\epsilon/\epsilon$ at $T_{min}(10\text{kHz}) \simeq 50$ mK, ensuring that $\delta\epsilon/\epsilon$ consists entirely of its resonant part. Gold capacitor electrodes were evaporated onto the sample. The dielectric constant was measured with a hand made bridge by comparison to a vacuum reference capacitor, that was placed on the one-kelvin pot of the dilution refrigerator. The AC-field was always kept within its linear response region.

Fig. 1 shows the evolution of $\delta\epsilon/\epsilon$ after a bias field of $F = 6.7$ MV/m was applied for two different waiting times of several hours ($t_w \gg t_s = 1$ s) at each of the temperatures $T = 10$ mK and $T = 20$ mK. The zero point of time ($t = 0$) is chosen to be at the completion of the bias field sweep and $\delta\epsilon/\epsilon = 0$ is defined as its initial value at zero field. The amplitude of $\delta\epsilon/\epsilon \sim 10^{-5}$ increases for longer waiting times and decreasing temperature as expected from (3). The dielectric constant decays approximately logarithmically over several decades in time justifying the simplification of describing relaxational processes by Heavyside Step Functions. Taking only the one-phonon process into account ($\alpha_0 = 0$) we would expect decay times of $\tau_0 \simeq 73t_w$ for $T = 10$ mK
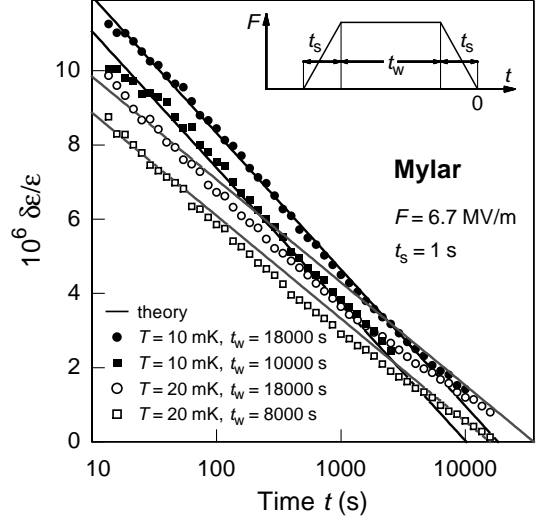

FIG. 1: Relative dielectric constant of Mylar after a bias field F was applied at two temperatures for very long waiting times $t_w \gg t_s$. All lines are theory curves after (3) (see text). The shematic indicates the application of the bias field and the choice of $t = 0$.

and $\tau_0 \simeq 37t_w$ for $T = 20$ mK according to (2). In contrast, our measurements suggest decay times in the order $\tau_0 \simeq t_w$ indicating the importance of interaction mediated relaxation [10]. Furthermore our experiments indicate that the restoration of the dipole gap takes longer for the higher temperature. According to (1) it is the interaction mediated relaxation process that results in an increasing relaxation time for the contributing TSs ($E_0 \sim k_B T$) with increasing temperature. Therefore our data unambiguously show that interaction mediated relaxation dominates in this temperature range.

One of the solid lines in Fig. 1 is a linear fit for $T = 10$ mK and $t_w = 18000$ s (filled circles). By comparison with (3) we find the fit-parameters $\tau_0/t_w \simeq 1.02$ and $P_0 U_0 \simeq 4.1 \cdot 10^{-4}$, the latter lying whithin typical estimations for other glasses[7]. The prefactor in (3) was previously obtained from the temperature variation of $\delta\epsilon/\epsilon$ well below T_{min} as $2P_0 \frac{2p^2}{3\varepsilon_0\varepsilon} \simeq 1.35 \cdot 10^{-4}$ [6, 11] and the dipole moment of the TSs in mylar was estimated to be $p \simeq 1.2$ Debye as discussed later (see fig. 4). Using (1) we estimate the temperature at which the interaction mediated relaxation time equals the one-phonon relaxation time as 55 mK $\lesssim T_c \lesssim$ 95 mK for $3 \gtrsim \tau_0/t_w \gtrsim 1$. Below T_c the interaction mediated relaxation dominates. The other three lines in fig. 1 are calculated from (3) using the same set of parameters. Our simplifying model agrees remarkably well with the data besides deviations from logarithmic decays particularly at the higher temperature.

In fig. 2 the restoration of the dipole gap at the temperature of $T = 10$ mK is displayed for 10 different waiting
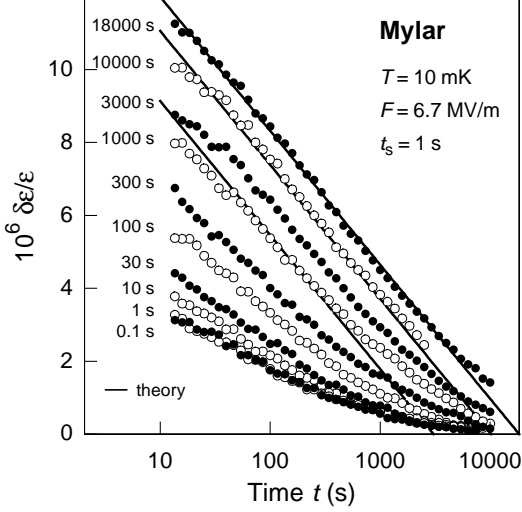
FIG. 2: Relative dielectric constant of Mylar after a bias field F was applied for waiting times t_w as marked left of each curve, while $t_s = 1$ s for all data. The solid lines are theory curves after (3) using the same parameters as in fig. 1.

FIG. 3: Relative dielectric constant of Mylar after a bias field F was applied for different t_s and t_w.

times between 0.1 s and 5 hours and otherwise the same conditions as for the data in fig. 1. The straight lines in fig. 2 are calculated from (3) for the three longest waiting times using the same parameters as for the theory curves in fig. 1. Our model which considers relaxation predicts parallel decay curves shifted along the logarithmic time axis proportional to $\ln(t_w)$. In experiments we observe this behaviour only for our longest waiting times (fig. 1). As t_w gets shorter $\delta\epsilon/\epsilon$ increasingly decays slower than expected, until for $t_w \lesssim t_s$ (our two shortest waiting times in fig. 2) the waiting time dependence disappears completely. To further investigate this puzzling effect we show in Fig. 3 the decay curves for 3 different sweep times at $t_w = 30$ s (solid points). As with longer t_w, $\delta\epsilon/\epsilon$ increases for longer t_s. For comparison we included the data points from Fig. 2 for $t_s = 1$ s and $t_w = 100$ s (open circles). Surprisingly their course is almost identical to the curve for $t_s = 10$ s and $t_w = 30$ s with a much smaller waiting time even if one were to make the obvious overestimation $t_w + 2t_s \rightarrow t_w$ to include relaxation while the bias field is being changed.

At this point we can safely conclude that at waiting times shorter than $t_w \sim 3000$ s an additional process gains importance that is not relaxational (due to waiting time independence) and instead depends on the sweep rate of the bias field. We propose that the changing electric (AC and DC) field drives TSs non-adiabatically during the bias field sweep, and that this process is responsible for the new behavior.

Let us consider the time dependent quantum mechanics of the TSs while the bias field is being changed. If the field sweep is 'slow' the TSs are driven adiabatically and their wave functions always adjust to the momentary
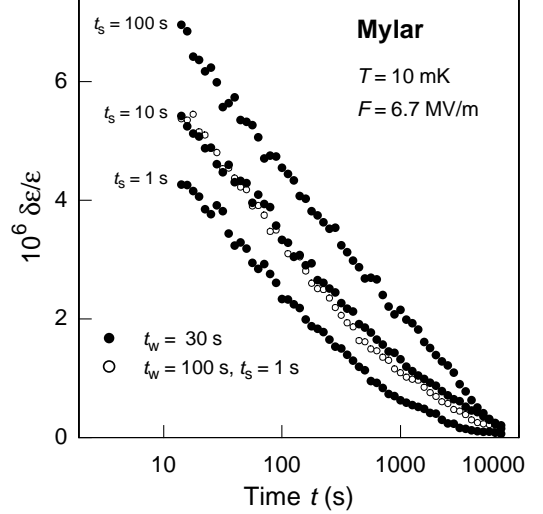
field. In the opposite case of a 'fast' sweep the TSs are driven non-adiabatically and their wave functions stay unchanged. These TSs remain in their original quantum states. Most TSs are asymmetric and therefore localized. In the following we consider non-adiabatically driven TSs having asymmetry energies that decrease to zero and successively increase again with changing field. For these TSs the original ground (excited) state at zero field converts into the excited (ground) state at maximum field. As the result the occupation numbers of these TSs are inverted. However, as the field is changed back to zero the non-adiabatically driven TSs are in their original state having been inverted twice. The Landau-Zener criterion [12] gives the probability

$$R_1(\Delta_0) = e^{-\left(\frac{\Delta_0}{\Delta_{0c}}\right)^2} \qquad \text{with} \quad \Delta_{0c} = \pi\sqrt{\Phi h/t_s} \quad (4)$$

with Plank's constant h that a system is driven non-adiabatically near $\Delta + \Phi = 0$. Only TSs with $\Delta_0 \sim \Delta_{0c}$ have a finite probability to have been inverted exactly once [13]. The non-adiabatically driven TSs have very long relaxation times $\tau(\Delta_{0c}, E_0)$ which are according to (1) and (4) proportional to $\tau \sim t_s/\Phi$. Neglecting the relaxational process leading to (2) we expect the decay time at which the dielectric constant reaches its initial value to be a function of t_s/Φ as well. However, the predicted decay would be non-logarithmic resembling a smoothened step occuring at the time $t \sim \tau(\Delta_{0c}, E_0 = k_B T)$.

An AC measuring field forces the dipole moment of a TS to oscillate with the measuring frequency ω as long as the quantum mechanical time evolution of the TS is able to follow the field. However, this description fails when the energy splitting E of a TS is smaller than a critical value $E_{AC} = \sqrt{\hbar\omega\, \mathbf{p} \cdot \mathbf{F}_{AC}}$ below which the AC-measuring field F_{AC} drives the system non-adiabatically.

TSs with $\Delta_0 < E_{AC}$ are driven nonadiabatically by the AC field for the time $\delta t^\star = t_s F_{AC}/F_{DC}$ in which $E < E_{AC}$. An initially localised TS will oscillate between the two wells during $\delta t^\star$ with a renormalized tunneling frequency $\widetilde{\Delta}_0/h$ [14]. Accordingly, TSs with $h\widetilde{\Delta}_0^{-1} > \delta t^\star$ stay localised in the original state whereas TSs with $h\widetilde{\Delta}_0^{-1} \ll \delta t^\star$ oscillate many times so that only half of them end up in their initial state. The AC-driving effect predicts a logarithmic decay with the decay time $\tau_0 \equiv \tau_0(\delta t^\star \sim t_s/\Phi)$ [15].

A combination of DC- and AC-driving explains the sweep time dependence visible in fig. 2 and 3 qualitatively. In our experiments $F_{AC} \simeq 9.7$ kV/m, resulting in $E_{AC} \sim \Delta_{0c}$ for $F_{DC} \simeq 6.7$ MV/m and $t_s = 1$ s. At longer t_s we expect AC-driving to increasingly become important at the expense of the DC-driving effect. The data in fig. 3 indicate a crossover from non-logarithmic to logarithmic behavior at $t_s \sim 10$ s. Consistently we did not observe a dependence on F_{AC} for $t_s \leq 10$ s (unpublished data) but have not searched for that effect for $t_s > 10$ s.
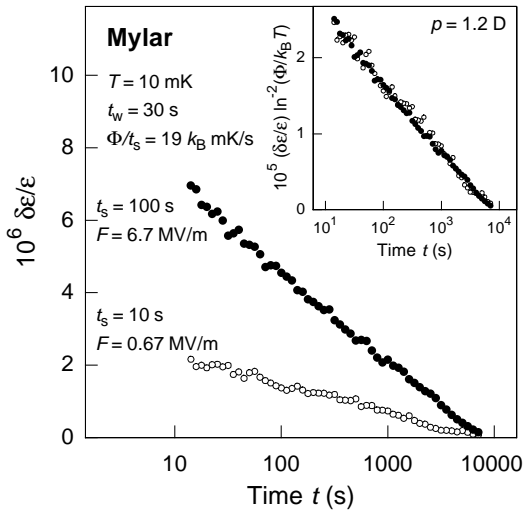

FIG. 4: Relative dielectric constant of Mylar after a bias field F was applied for the same sweep rate, the same waiting time but different bias field strengths and sweep times. In the inset the data are normalized with respect to their bias field for the dipole moment of $p = 1.2$ D.

Our model including non-adiabatic driving predicts $\tau_0 \equiv \tau_0(t_s/\Phi_{DC})$. In fig. 4 we plot two data sets with the same $\Phi/t_s = 19\ k_B$mK/s but different sweep times and bias fields. The decay times of both data curves are the same as expected. We stress that relaxational processes during t_w cause a decay time $\tau_0 \sim t_w$ (fig. 1), but in fig. 4 $\tau_0 \gg t_w$ and thus the decay is due to the driving effect. In our model this can be understood by recognizing that the finite waiting time necessarily implies a smallest Δ_0 for TSs that can possibly decay while the bias field is applied. This smallest Δ_0 is larger than Δ_{0c} unless $t_w \gg t_s$. Regardless of which effect breaks the

strongly coupled clusters of TSs, we always find the temperature dependence of the decay of the dielectric constant propotional to $[\ln(\Phi/k_B T)]^2$. This is a consequence of the central assumption in the dipole gap model that only TSs with energy splitting $T \lesssim E_0 \lesssim \Phi$ contribute to changes in the dielectric constant [8]. Using this dependence we normalized the two data sets as shown in the inset in fig. 4. Very good agreement was reached with the dipole moment $p \simeq 1.2$ Debye (that was used for the theory curves in fig. 1 and 2).

We have investigated the dynamics of the destruction and the restoration of the zero field dipole gap by application of strong electric bias fields. Only our data curves at very long waiting times $t_w \gg t_s$ can be explained by solely relaxational processes. Our investigation suggests non-adiabatic driving of the TSs as a possible reason for the destruction of the dipole gap for shorter t_w. Furthermore we have shown that at temperatures below 50 mK the relaxation of TSs is dominately by a relaxation mechanism due to interactions between TSs [8].

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